Global Optimization of Chemical Processes using Stochastic Algorithms

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Abstract. Many systems in chemical engineering are difficult to optimize using gradient-based algorithms. These include process models with multimodal objective functions and discontinuities. Herein, a stochastic algorithm is applied for the optimal design of a fermentation process, to determine multiphase equilibria, for the optimal control of a penicillin reactor, for the optimal control of a non-differentiable system, and for the optimization of a catalyst blend in a tubular reactor. The advantages of the algorithm for the efficient and reliable location of global optima are examined. The properties of these algorithms, as applied to chemical processes, are considered, with emphasis on the ease of handling constraints and the ease of implementation and interpretation of results. For the five processes, the efficiency of computation is improved compared with selected stochastic and deterministic algorithms. Results closer to the global optimum are reported for the optimal control of the penicillin reactor and the non-differentiable system.

1. INTRODUCTION

Gradient-based optimization algorithms are known to converge to local optima. Besides, they cannot be applied to non-differentiable problems, although subgradient-based algorithms can, in certain cases, circumvent non-differentiability problems. To surmount these difficulties, stochastic optimization methods, also called adaptive random search (ARS) or random direct search methods, have been widely used in the engineering optimization literature. An introductory review is given by Reklaitis et al. (1983), with convergence proofs provided for stochastic algorithms by several authors (Devroye, 1978; Solis and Wets, 1981; Gelfand and Mitter, 1991).

Luus and Jaakola (1973) proposed the LJ random search method and successfully solved a number of optimization problems in mathematics and chemical engineering. The algorithm was later improved (Wang and Luus, 1978) to increase its reliability in locating the global optimum. Several authors have proposed modified versions of the LJ method, with detailed discussions given by Salcedo et al. (1990) and Salcedo (1992). Despite its simplicity, the LJ algorithm still remains a versatile and reliable method (Spaans and Luus, 1992; Luus, 1993d), though it usually requires a large number of function evaluations.

Several attempts have been made to develop more efficient ARS algorithms. Goulcher and Casares (1978) developed the Controlled Random Search (CRS) method, that has proven to be very robust and especially efficient in achieving the global optimum within 0.1 %. Other ARS methods reported to be more efficient than the

LJ method are the ARDS (Martin and Gaddy, 1982), the MMA (Mihail and Maria, 1986) and the SGA method (Salcedo et al., 1990). However, the CRS method has the advantage of requiring less procedural (heuristic) parameters, and hence, it is especially convenient for multimodal objective functions, where the starting values for the parameters are critical.

Masri et al. (1980) presented a random-search algorithm, similar to the CRS algorithm, that is very efficient for global optimization. This algorithm has solved a number of complex problems related to mechanical engineering, automatic control, and image processing (Bekey and Masri, 1983; Pronzato et al., 1984).

The CRS algorithm, in its original form, could only be applied to problems where the equality constraints can be solved sequentially. It was improved by Banga and Casares (1987) with the addition of a tearing algorithm to decompose the equality constraints and a modified Newton-Raphson algorithm for the solution of the remaining subsets of equality constraints. The resulting Integrated Controlled Random Search (ICRS) method has successfully solved several complex multimodal systems (Casares and Banga, 1989).

Kirkpatrick et al. (1983) proposed the simulated annealing (SA) algorithm, which has become extremely popular for the solution of combinatorial optimization problems (Ingber, 1993). SA has been applied successfully to an enormous variety of combinatorial problems, some in chemical engineering (Dolan et al, 1989; Ku and Karimi, 1991; Huber, 1994; Floquet et al., 1994). Genetic algorithms (GA) have also become widely used for these problems (Davis, 1989; Goldberg, 1989), with applications in chemically-related fields like computer-aided molecular design (Venkatasubramanian et al., 1994).

More efficient versions of the SA algorithm have been presented (Ingber, 1989; Moscato and Fontanari, 1990) to reduce the enormous computational effort. However, although SA versions for continuous global optimization have been developed (Vanderbilt and Louie, 1984; Corana et al., 1987), they require many function evaluations, and hence, the ARS methods are much preferred for continuous optimization problems.

1.1. Dynamic Optimization (Optimal Control) of Chemical Processes

The control of batch and semi-batch chemical processes is a challenging dynamic optimization problem that is usually difficult to solve because of nonlinear system dynamics and constraints on the control and state variables (Cuthrell and Biegler, 1989; Luus, 1993a,b). Besides, the global optimum is often difficult to determine due to the insensitivity of the performance index to the control profiles (Seider et al., 1991).

Many authors have used the Maximum Principle of Pontryagin to solve optimal control problems (OCPs), but this approach may be difficult to implement due to state constraints and other complexities, so alternative methods have been proposed. Cuthrell and Biegler (1989) present a method based on orthogonal collocation on finite elements and successive quadratic programming (SQP), and apply it to a fed-batch fermentor for the production of penicillin. Chen and Hwang (1990) criticize this approach, and propose a method based on piecewise-constant control parameterization to convert the original problem into a sequence of finite-dimensional nonlinear programming problems (NLPs) that are solved by a SQP algorithm. To illustrate this method, they solve an OCP for the fed-batch fermentation of ethanol.

Luus (1993a,b,c) improves on the results of Cuthrell and Biegler (1989) and Chen and Hwang (1990) through the use of penalty functions together with his Iterative Dynamic Programming (IDP) method. He indicates that the NLP approaches used by these authors may converge to local optima unless the initial control profiles are very close to the global optimum. However, he recognizes that more research is needed on the convergence properties of the IDP method especially when many penalty functions are used. Besides, the use of penalty functions requires several preparatory runs to estimate the penalty factors that ensure all of the constraints are satisfied.

Direct search methods have also been used to solve OCPs (Umeda et al., 1972; Biegler, 1984; Banga et al., 1991; Bojkov et al., 1993), though not all of these methods perform similarly. The ICRS/DS (Integrated Controlled Random Search for Dynamic Systems) method is an extension of the ICRS method that has been effective for the solution of the OCPs for fed-batch bioreactors and other complex bioprocesses (Banga et al., 1991; Banga et al., 1994). It is based on the parameterization of the control variables using variable- length, piecewise-linear polynomials and the solution of the resulting NLP using the stochastic algorithm of Banga and Casares (1987). For each profile of the control variables, the system equations are integrated using a differential-algebraic equation solver. This method is simple to implement, and can solve difficult OCPs with reasonable computation effort. It is especially reliable when optimizing multimodal systems, like fed-batch fermentors. Moreover, convergence is assured in all cases, even for poorly-scaled systems and independently of the starting control profiles.

In this paper, the advantages of the ICRS algorithm (for steady state systems) and the ICRS/DS algorithm (for dynamic systems) for solving several complex (multimodal) continuous optimization problems related to chemical engineering are demonstrated.

2. CONSTRAINED NLP AND ICRS ALGORITHM

The general form of the constrained nonlinear program is:

$$\min_{\mathbf{X}} F\{\mathbf{X}\} \tag{1}$$

Subject to:

$$\mathbf{H}\{\mathbf{X}\} = 0 \tag{2}$$

$$\mathbf{G}\{\mathbf{X}\} \leq 0 \tag{3}$$

where, in chemical engineering, the equality constraints, $\mathbf{H}$, are usually the mass, energy and momentum balances in the steady state, and the inequality constraints, $\mathbf{G}$, are usually the design and process specifications.

The ICRS algorithm (Banga and Casares, 1987) consists of an algorithm to efficiently structure and order the equality constraints, plus an improved version of the CRS algorithm (Goulcher and Casares, 1978). In the preliminary stage of a two-stage algorithm, the tearing algorithms of Book and Ramirez (1976, 1984) reduce the number of equality constraints to be solved simultaneously. An occurrence matrix is formed using a special parser and rearranged, yielding a set of specifications that permit the unknowns to be calculated sequentially. When necessary, subsets of equality constraints are solved simultaneously. Potential problems are encountered near singular points, in nonlinear regions or where the values of the decision variables yield a near-singular Jacobian matrix, but, thus far, they have not occurred in the systems examined.

In a second stage, the CRS algorithm searches for the optimum, beginning with a user-specified initial point, though it may generate a feasible initial point automatically if required. New points at each iteration are generated using a Gaussian probability distribution, in which the standard-deviation vector (equivalent to the search step size of other methods) is calculated as a function of the decision variables vector, lower and upper bounds on the decision variables and a heuristic parameter k_1 (default $k_1 = 1/3$). To test the feasibility of each new point, the equality constraints are solved, and the inequality constraints are checked. A modified Newton-Raphson algorithm is used to solve the simultaneous equality constraints.

When no progress is made after a specified number of trials, the standard deviation vector is reduced through multiplication by a second heuristic parameter, k_2 (default $k_2 = 1/2$). The number of trials is taken as $\eta_e \cdot n$, where n is the number of decision variables and η_e is a third heuristic parameter (default 25). When a feasible point that improves the objective function is found, a new iteration is started, updating the elements of the standard deviation vector. The convergence criterion is based upon pre-specified tolerances for the objective function and decision variables. A MATLAB implementation of the basic CRS algorithm is given in Appendix A.

3. THE DYNAMIC OPTIMIZATION (OPTIMAL CONTROL) PROBLEM

The models for most batch or semi-batch chemical processes are comprised of differential-algebraic equations. When the terminal time is fixed, the OCP can be stated:

Find $\mathbf{u}\{t\}$ over $t \in [t_0, t_f]$ to minimize (or maximize):

$$J[\mathbf{x},\mathbf{u}] = \Theta[\mathbf{x}\{t_f\}] + \int_{t_0}^{t_f} \Phi[\mathbf{x}\{t\},\mathbf{u}\{t\},t]\,dt \qquad (4)$$

Subject to:

$$\frac{d\mathbf{x}}{dt} = \Psi\left[\mathbf{x}\left\{t\right\}, \mathbf{u}\left\{t\right\}, t\right] \tag{5}$$

$$\mathbf{x}\left\{t_0\right\} = \mathbf{x}_0 \tag{6}$$

$$\mathbf{h}\left[\mathbf{x}\left\{t\right\}, \mathbf{u}\left\{t\right\}\right] = 0 \tag{7}$$

$$\mathbf{g}\left[\mathbf{x}\left\{t\right\}, \mathbf{u}\left\{t\right\}\right] \leq 0 \tag{8}$$

$$\mathbf{x}^L \leq \mathbf{x}\left\{t\right\} \leq \mathbf{x}^U \tag{9}$$

$$\mathbf{u}^L \leq \mathbf{u}\left\{t\right\} \leq \mathbf{u}^U \tag{10}$$

where J is the performance index, $\mathbf{x}$ is the vector of state variables, $\mathbf{u}$ the vector of control variables, Eqn. (5) is the system of ordinary-differential equality constraints, Eqn. (6) the initial conditions for Eqn. (5), Eqns. (7) and (8) are the equality and inequality algebraic constraints and Eqns (9) and (10) are the upper and lower bounds on the state and control variables. The system is assumed to be lumped; that is, modeled by ordinary differential equations (ODEs).

When the system is distributed (e.g., an immobilized-enzyme bioreactor, or a solids dehydrator), the partial differential equations (PDEs) can be transformed into a system of ODEs using the numerical method of lines (Schiesser, 1991), or into a system of nonlinear equations without derivatives using finite differences or finite elements (Banga et al., 1994). Therefore, the OCP above applies for distributed systems. When the terminal time is free, $\mathbf{u}\left\{t\right\}$ and t_f must be determined. This problem can be solved by tearing t_f and solving the OCP above iteratively.

4. ICRS/DS: A STOCHASTIC DYNAMIC OPTIMIZATION ALGORITHM

As mentioned above, the OCP is transformed using a simple yet flexible parameterization of the control vectors, $\mathbf{u}\left\{t\right\}$, over $t \in [t_0, t_f]$ using N_p points. The value of $\mathbf{u}\left\{t\right\}$ can be calculated using several types of interpolation, including piecewise constant, piecewise linear, B-splines and Lagrange polynomials. After several studies, variable-length piecewise-linear interpolation appears to give the best results. The resulting NLP has $2 \cdot N_p \cdot M$ decision variables where M is the number of control variables. Despite its simplicity, this procedure has proven to be very reliable and efficient.

For most chemical processes, the differential-algebraic equations (DAEs) are stiff during some portion of the time domain, so a robust and efficient initial-value integrator must be used. In this work, DASSL (Petzold, 1982; Brenan et al., 1989) has been used with excellent results in all cases. With this approach, no preparation or modification of the original DAEs is required, and hence, the method is easy to implement, as described below. This procedure successfully solved several complex OCPs involving distributed parameters (Banga et al., 1991; Banga et al., 1994).

When the process is modelled as a split-boundary-value problem, with boundary conditions at t_0 and t_f, the ODEs can be discretized using orthogonal collocation on finite elements (or a similar method) and the ICRS algorithm applied to the resulting nonlinear equations. In this case, the state variables at the mesh points would be adjusted stochastically. Note that, to our knowledge, the effectiveness of this methodology has not yet been examined.

4.1. Implementation of the ICRS/DS algorithm

To implement the ICRS/DS algorithm, only a function declaring the differential-algebraic constraints, Eqns. (5) and (7), and a second function, where the inequality constraints, Eqns. (8) and (9) are checked (e.g., using if...then conditionals), and the performance index, Eqn. (4), calculated, are needed. Note that it is desirable, but not necessary, to provide a function for the analytical differentiation of the elements of the Jacobian matrices. With analytical derivatives, DASSL is usually far more efficient.

There is no need to transform the original problem, even when it is poorly scaled. There is also no need to define penalty functions and calculate their weights, because constraints are handled directly. Besides, the method is not gradient based, so non-differentiable systems can be solved. These factors make this procedure very attractive. Other methods often require substantial time and expertise to prepare a suitable algorithm. Furthermore, the ICRS/DS algorithm is simple to code in different languages and/or environments, provided that access to DASSL is available. In this context, recent tools like OCTAVE (Eaton, 1994) may facilitate its even more widespread usage.

5. CASE STUDIES

Five case studies are examined in this work. In this section, the optimization problems are formulated. The results are presented and discussed in the next section.

5.1. Case study I: Optimal design of a fermentation process

This is a design problem studied by Brengel and Seider (1992) and Sun (1993). The flowsheet contains a well-stirred, aerobic fermentor in which *Saccharomyces cerevisiae* grows in a medium of sugar cane molasses and a centrifuge for recovery of the cell mass, as illustrated in Figure 1. The fermentor product contains cell mass and substrate in concentrations X and S, respectively. After centrifugation, a fraction (α) of the dilute substrate is recycled to the fermentor. The constrained NLP is formulated, assuming steady-state operation, to maximize the venture profit, ϕ, by adjusting seven independent variables:

$$\max_{h,X,S,\alpha,F_c,F,f_v} \phi = P - ROR \cdot FCI \tag{11}$$

Subject to:

$$\begin{aligned}
\frac{F + F_c - (1-\alpha) f_v h^{0.5}}{\pi R^2} &= 0 && (12)\\
\frac{-X\left(F + F_c + \alpha f_v h^{0.5}\right)}{\pi R^2 h} + kXSe^{\frac{-S}{K}} &= 0 && (13)\\
\frac{F(S_F - S) + F_c(S_c - S)}{\pi R^2 h} - \frac{kXSe^{\frac{-S}{K}}}{a+bS} &= 0 && (14)\\
1.9R - h &\geq 0 && (15)\\
\alpha &\geq 0 && (16)\\
F_c &\geq 0 && (17)\\
F &\geq 0 && (18)
\end{aligned}$$

with:

$$P\left(\$10^7/yr\right) = 1.0 \cdot 10^{-7}\left(c_1 X f_v h^{0.5} - c_2 F - c_3 F_c - c_4 X f_v h^{0.5}/3600\right) P_t$$
$$FCI\left(\$10^7\right) = 1.18 \cdot 10^{-7}\left(F_{bm,v} B_v V^{0.724} + F_{bm,c} B_c \left(X f_v h^{0.5}\right)^{0.444}\right)$$
$$P_t\,(\text{operating minutes}/yr) = 504,000$$
$$ROR = 0.15$$

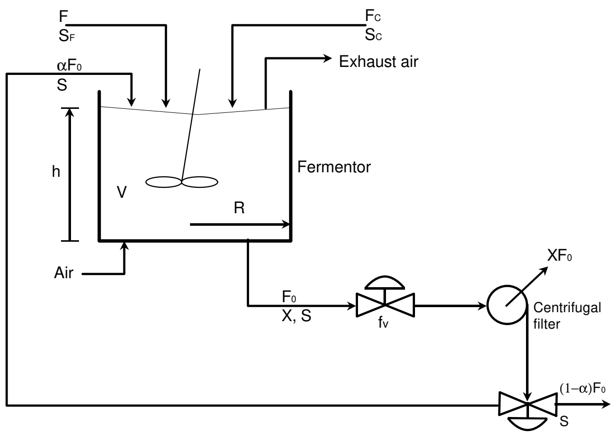

Figure 1. Flowsheet of the fermentation process. Reprinted from Brengel and Seider (1992).

where the equality constraints are the mass balances, F and S_F are the flow rate and substrate concentration of the feed (F_c and S_c of the concentrated feed), h, R and V are the height, radius and volume of the liquid holdup in the fermentor, f_v is the valve constant, k, K, a and b are constants in the kinetics model, c_1, ..., c_4 are cost coefficients, B and F are base cost and bare module factors for the fermentor and centrifuge, FCI is the fixed capital investment, ROR is the rate of return on investment, and the inequality constraints consist of one design specification and three non-negativity constraints.

5.2. Case study II: Multiphase equilibria

When a mixture is at equilibrium at a given temperature and pressure, the Gibbs free energy is at the global minimum subject to mass balances constraints. As the models that describe non-ideal mixtures are highly nonlinear, the objective function is usually multimodal. Here, liquid-liquid equilibrium for a binary, two-phase mixture (Sun and Seider, 1992; Sun, 1993) is considered. The constrained NLP, written in terms of mole fractions, is:

$$\begin{aligned}\min_{x_{i\ell},\beta} \frac{\Delta G^m}{n^f RT} &= \beta\left(x_{11} ln x_{11}\gamma_{11} + x_{21} ln x_{21}\gamma_{21}\right) + \\ &\quad (1-\beta)\left(x_{12} ln x_{12}\gamma_{12} + x_{22} ln x_{22}\gamma_{22}\right) \qquad (19)\end{aligned}$$

Subject to:

$$\begin{aligned} z_1 - [\beta x_{11} + (1-\beta)\, x_{12}] &= 0 \qquad (20)\\ x_{1\ell} + x_{2\ell} - 1 &= 0 \qquad (21)\\ x_{i\ell} &\geq 0 \qquad (22)\\ \beta &\geq 0 \qquad (23)\\ 1-\beta &\geq 0 \qquad (24)\end{aligned}$$

with $\ell = 1,2$ and $\forall i,\ell$, and where $x_{i\ell}$ is the mole fraction of species i in phase ℓ, β is the feed fraction in the first liquid phase, and z_i is the mole fraction of species i in the feed. The activity coefficient for species i in phase $\ell, \gamma_{i,\ell}$, is considered to be a function of the mole fractions in phase ℓ only. Sun and Seider (1992) considered an equimolar mixture of n-butylacetate ($i = 1$) and water ($i = 2$), using the NRTL equation for the activity coefficients (with $\tau_{12} = 3.00498$, $\tau_{12} = 4.69071$, and $\alpha_{12} = \alpha_{21} = 0.391965$).

5.3. Case study III: Optimal control of a fed-batch fermentor for penicillin production.

This is the model of a fed-batch fermentor for the production of penicillin, as studied by Lim et al. (1986) and revised by Cuthrell and Biegler (1989). The same problem was studied by Luus (1993b,c) using Iterative Dynamic Programming. Van Impe et al. (1992) studied the optimal control utilizing a modified unstructured model.

The objective function is to maximize the amount of penicillin produced using the feed rate as the control variable, as shown in the OCP below (Luus, 1993b):

Find $\mathbf{u}\{t\}$ and t_f over $t \in [t_0, t_f]$ to maximize $J = x_2\{t_f\}\, x_4\{t_f\}$

Subject to:

$$\frac{dx_1}{dt} = h_1 x_1 - u\left(\frac{x_1}{500x_4}\right) \tag{25}$$

$$\frac{dx_2}{dt} = h_2 x_1 - 0.01x_2 - u\left(\frac{x_2}{500x_4}\right) \tag{26}$$

$$\frac{dx_3}{dt} = -\frac{h_1 x_1}{0.47} - h_2\frac{x_1}{1.2} - x_1\left(\frac{0.029x_3}{0.0001 + x_3}\right) + \frac{u}{x_4}\left(1 - \frac{x_3}{500}\right) \tag{27}$$

$$\frac{dx_4}{dt} = \frac{u}{500} \tag{28}$$

$$h_1 = 0.11\left(\frac{x_3}{0.006x_1 + x_3}\right) \tag{29}$$

$$h_2 = 0.0055\left(\frac{x_3}{0.0001 + x_3\left(1 + 10x_3\right)}\right) \tag{30}$$

where x_1, x_2, and x_3 are the biomass, penicillin and substrate concentrations, and x_4 is the volume. The initial conditions are:

$$\mathbf{x}\{t_0\} = [\ 1.5\ 0\ 0\ 7]^T \tag{31}$$

The upper and lower bounds on the state variables (path constraints) are (Case III of Cuthrell and Biegler, 1989):

$$0 \leq\ x_1\ \leq 40 \tag{32}$$

$$0 \leq\ x_3\ \leq 25 \tag{33}$$

$$0 \leq\ x_4\ \leq 10 \tag{34}$$

The upper and lower bounds on the feed rate are:

$$0 \leq\ u\ \leq 50 \tag{35}$$

5.4. Case study IV: Optimal control of a non-differentiable system.

This problem has been studied by Thomopoulos and Papadakis (1991), who report convergence difficulties using several optimization algorithms, and by Luus (1993c), using Iterative Dynamic Programming. The optimal control problem is:

Find $\mathbf{u}\{t\}$ to minimize $J = x_3\{t_f\}$
Subject to:

$$\frac{dx_1}{dt} = x_2 \tag{36}$$
$$\frac{dx_2}{dt} = -x_1 - x_2 + u + d \tag{37}$$
$$\frac{dx_3}{dt} = 5x_1^2 + 2.5x_2^2 + 0.5u^2 \tag{38}$$

with

$$d = 100\,[U\{t-0.5\} - U\{t-0.6\}] \tag{39}$$

where $U\{t-\alpha\}$ is the unit function such that $U = 0$ for $t-\alpha < 0$ and $U = 1$ for $t-\alpha > 0$. Hence d is a rectangular pulse of magnitude 100 from t=0.5 until t=0.6. These authors consider $t_f = 2.0\ s$, and the initial conditions:

$$\mathbf{x}\{t_0\} = [\ 0\ 0\ 0]^T \tag{40}$$

5.5. Case study V: Global optimization of a bifunctional catalyst blend in a tubular reactor.

Luus et al. (1992) and Luus and Bojkov (1994) consider the optimization of a tubular reactor in which methylcyclopentane is converted into benzene. The blend of two catalysts, for hydrogenation and isomerization, is described by the mass fraction u of the hydrogenation catalyst. The optimal control problem is to find the catalyst blend along the length of the reactor (defined using a characteristic reaction time, t, in the interval $0 \leq t \leq t_f$, where $t_f = 2000\ g \cdot h/mol$, corresponding to the reactor exit) such that the benzene concentration at the exit of the reactor is maximized:

Find $\mathbf{u}\{t\}$ to maximize $J = x_7\{t_f\}$

Subject to:

$$\frac{dx_1}{dt} = -k_1 x_1 \tag{41}$$
$$\frac{dx_2}{dt} = k_1 x_1 - (k_2 + k_3)\, x_2 + k_4 x_5 \tag{42}$$

$$\frac{dx_3}{dt} = k_2 x_2 \tag{43}$$

$$\frac{dx_4}{dt} = -k_6 x_4 + k_5 x_5 \tag{44}$$

$$\begin{aligned}\frac{dx_5}{dt} &= k_3 x_2 + k_6 x_4 - (k_4 + k_5 + k_8 + k_9)\, x_5 + \\ &\quad k_7 x_6 + k_{10} x_7\end{aligned} \tag{45}$$

$$\frac{dx_6}{dt} = k_8 x_5 - k_7 x_6 \tag{46}$$

$$\frac{dx_7}{dt} = k_9 x_5 - k_{10} x_7 \tag{47}$$

where x_i, $i = 1, ...7$, are the mole fractions of the chemical species ($i = 1$ for methylcyclopentane, $i = 7$ for benzene), the rate constants are functions of the catalyst blend $\mathbf{u}\{t\}$:

$$k_i = c_{i1} + c_{i2} u + c_{i3} u^2 + c_{i4} u^3 \qquad i = 1, 2, ..., 10 \tag{48}$$

and the coefficients c_{ij} are given by Luus et al. (1992). The upper and lower bounds on the mass fraction of the hydrogenation catalyst are:

$$0.6 \leq u \leq 0.9 \tag{49}$$

The initial vector of mole fractions is:

$$\mathbf{x}^T \{t_0\} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{50}$$

6. RESULTS AND DISCUSSION

6.1. Case study I:

Brengel and Seider (1992) solved the Kuhn-Tucker conditions, with the equations of complementary slackness replaced by the Mangasarian equations, using a Newton homotopy-continuation algorithm. They showed that three solution branches exist as the cost coefficient of the concentrated feed stream (c_3) is varied. Sun (1993) used this formulation and a Newton homotopy-continuation method to seek multiple solutions along a single homotopy path at $c_3 = 150$, and found a global optimum with $\phi\left(\$10^7/yr\right) = 11.5899$. She reported that the convergence to multiple stationary points along a single homotopy path was sensitive to the initial values of some of the variables. Furthermore, numerical problems and excessive computation times near turning points were reported.

When the preliminary stage of the ICRS algorithm was applied, the occurrence matrix of the equality constraints indicated that sequential solution is possible taking h, F_c, F and S as decision variables and solving constraints (14), (13) and (12) seriatim, obtaining X, f_v and α. In the second stage of the ICRS algorithm, convergence to the global optimum was achieved in all cases, starting from different initial points and using different sets of upper and lower bounds on the decision variables. For example, starting from:

$\mathbf{X}^0 = [\ h\ F_c\ F\ S]^0 = [\ 5.0\ 2.0\ 1.0\ 0.3]$

with a corresponding $\phi^0 = 5.2634$, the ICRS algorithm converged to:

$\phi^* = 11.5840$, with $\mathbf{X}^* = [\ 5.700\ 3.751\ 0.0018\ 0.3111]$

which is only 0.05 % from the global optimum found by Sun (1993), $\phi^* = 11.5899$. It should be noted that convergence to 1% from the global optimum was very rapid (25 iterations), but further refinement to reach 0.05% from the optimum took many more iterations. However, for most design problems, such a tight tolerance is not needed.

To compare the performance of the ICRS algorithm with other stochastic algorithms, the LJ algorithm (Luus and Jaakola, 1973; Wang and Luus, 1978) was implemented. Convergence to the global optimum was achieved in all cases, but the computational effort was 2-4 times greater. Convergence to tolerances of 0.05% was also very slow.

Finally, the Sequential Quadratic Programming (SQP) algorithm was utilized. The version used was that implemented in the MATLAB Optimization Toolbox, based on Han (1977), Powell (1978) and Gill et al. (1981). This algorithm did not converge except when the global optimum found by the ICRS algorithm (tolerance of 0.05%) was used as the initial point. It may be possible to circumvent this by scaling the functions and variables, a procedure that is not necessary when implementing the stochastic algorithms.

6.2. Case study II:

Sun and Seider (1992) used the Newton homotopy-continuation method to locate all of the stationary points. For an equimolar ($\mathbf{z}^T = [\ 0.5\ 0.5]$) feed of n-butylacetate and water, they found the global optimum at:

$x_{11} = 0.004557, x_{21} = 0.995443, x_{12} = 0.59199, x_{22} = 0.40801, \beta = 0.15659$

They report that, initializing the Lagrange multipliers with positive numbers, all four of the solutions reside on the homotopy path. Three do not have physical significance and the fourth is at the global minimum of the Gibbs free energy.

When the ICRS algorithm is applied, in the first stage, Equations (20) and (21), with $\ell = 1, 2$, are solved in seriatim taking x_{11} and x_{12} as decision variables. The implementation is, again, straightforward, as no further transformation or preparation of the equations is needed.

Starting from the initial point $\{x_{11}^0 = 0.65, x_{12}^0 = 0.4\}$, and using the default values for the heuristic parameters ($k_1 = 1/3, k_2 = 1/2, \eta_e = 25$), convergence to the global optimum $\{x_{11} = 0.00455, x_{12} = 0.5919\}$ was rapid. However, when additional runs, starting from the same initial point, were made to confirm the reliability of the method, convergence to local optima was found in many cases. After completing more runs, a success ratio (SR) of only 35% was calculated. Starting from other initial points, with the same default values for the heuristic parameters, SRs between 10 and 60% were found.

To improve upon this disappointing result, the effect of the parameter k_1 on the SR was studied. It should be noted that the default value ($k_1 = 1/3$) is effective for mildly multimodal systems. With $k_1 = 1$, the SR was doubled for the initial point $\left\{x_{11}^0 = 0.65, x_{12}^0 = 0.4\right\}$. When $k_1 = 2$ was used, $SR = 97\%$ was calculated, with only a slight increment of the computational effort.

With this minor modification, the ICRS algorithm showed high reliability and efficiency, especially considering the difficulty of calculating multiphase equilibria. However, the reliability and efficiency of the algorithm should be compared with the methods of Michelsen (1982a,b), Sun and Seider (1995) and McDonald and Floudas (1994a-e). Note that the latter algorithm is guaranteed to locate the global minimum for mixtures that utilize the NRTL, UNIQUAC, Wilson, UNIFAC and ASOG models. However, it has been specially taylored to solve this type of global optimization problem while ICRS can be applied to any problem without transformations. Finally, the ICRS algorithm should be evaluated for more complex multiphase equilibria (e.g., vapor-liquid-liquid and liquid-liquid- liquid equilibria) where the phase distribution is sensitive to the temperature, pressure and composition.

6.3. Case study III:

To compare the results using the ICRS algorithm with those of Luus (1993b), the OCP was solved for $t_f = 126h$, with a constant starting profile, $\mathbf{u}^0\,\{t\} = 11.9$. No convergence difficulties were found. Tight tolerances (10^{-7} for absolute and relative tolerances) were used in DASSL.

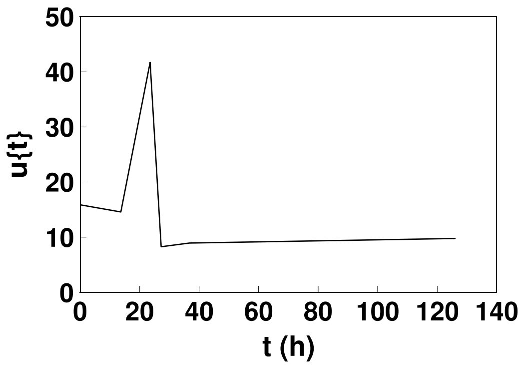

Figure 2. Optimal feed rate profile for case study III, with $t_f = 126h$. The associated performance index is $J = 87.78$.

The optimal control profile is shown in Figure 2, with the state variables profiles in Figure 3. The performance index is $J = 87.78$, slightly better than the one reported by Luus (see Table 1). Note that the control profile is parameterized using variable-length piecewise linear polynomials, and consequently, when the optimal control profile is nonlinear, the ICRS algorithm converges to sub-optima, which are, however, very close to the global optimum. In Figure 4(a), the improvement of the performance index as a function of the iteration number is shown for a typical run. The ICRS/DS algorithm required only 15 iterations to arrive at these results.

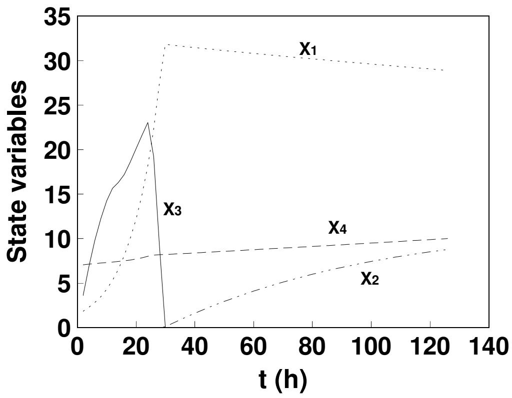

Figure 3. State variable profiles for case study III at the optimal control profile shown in Figure 2.

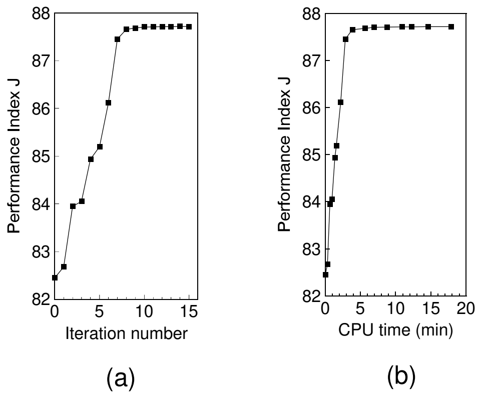

Figure 4. Case study III: (a) Performance index as a function of iteration number. (b) Performance index as a function of computing time (i486/50 PC).

Table 1. Performance index for case study III (penicillin production).

	Performance index J	
	$t_f = 126h$	$t_f = 132h$
Cuthrell and Biegler (1989)	-	87.69
Luus (1993b)	87.76	87.95
Luus (1993c)	-	87.85
Present study	87.78	87.90

To quantify the computational effort, the improvement in the performance index as a function of the CPU time is shown in Figure 4(b). The calculations were done in double precision, using MS 5.1 Fortran 77 and a PC i486/50MHz. The total computation time was 18 min., although the performance index is 87.70, within 0.1 % of the final optimum, after only five minutes. Luus (1993b) reported computation times ranging from 1.7 to 2.5 h using a PC i486/33MHz.

Therefore, the ICRS/DS algorithm appears to be more efficient. Since the ICRS/DS algorithm is stochastic, different seed values of the pseudo-random number generator result in different computation times. For this case study, and the initial constant profile, $\mathbf{u}^0\{t\} = 11.9$, the CPU times ranged from 10 to 40 min.

To find the global optimum, the OCP was solved for other t_f values. The best performance index, $J = 87.90$, was found for $t_f = 132h$, in close agreement with previous results. Note that the performance index in Table 1 is very close to that reported by Luus (1993b), and slightly better than those reported by Luus(1993c) and Cuthrell and Biegler (1989), who reported convergence problems. This is probably due to the insensitivity of J to the control profile at short times. However, no convergence problems were encountered using the ICRS/DS algorithm.

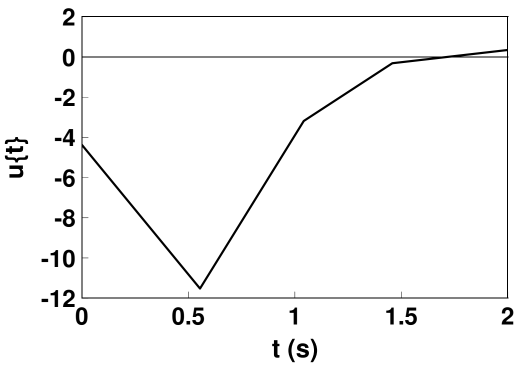

Figure 5. Optimal control for case study IV. The associated performance index is J=58.13.

6.4. Case study IV:

Thomopoulos and Papadakis (1991), using an exponential smoothing procedure to handle the discontinuities at $t = 0.5$ and $t = 0.6$, found a minimum of $J = 58.538$. They reported convergence problems for several optimization algorithms. Using IDP, Luus (1993c) found an optimal control with a minimum of $J = 58.18$.

Using the ICRS/DS algorithm, no convergence difficulties were encountered. The optimal control profile is shown in Figure 5, with $J = 58.13$, slightly less than those previously reported. It must be emphasized that the implementation of the ICRS/DS algorithm for this non-differentiable problem is straightforward, as in the other case studies.

6.5. Case study V:

Luus et al. (1992) and Luus and Bojkov (1994) have shown that the global optimimization of the bifunctional catalyst blend in a tubular reactor is very difficult due to the large number of local optima. In fact, Luus et al. (1992) report that, using SQP and 100 starting points, 25 local optima were found (with $8.113 \leq J \leq 10.053$), and the global optimum could not be obtained. Storey (1992) could not obtain the global optimum using several methods: modified controlled random search, multilevel linkage and simulated annealing. Using IDP, Luus et al. (1992) found the global optimum, with $J = 10.0942 \cdot 10^{-3}$, and two additional local optima. Luus and Bojkov (1994) studied the effect of several parameters of the IDP method on the likelihood of finding the global solution, with success ratios (SRs) between 75 and 95 %, and CPU times between 19 and 40 minutes (PC i486/33).

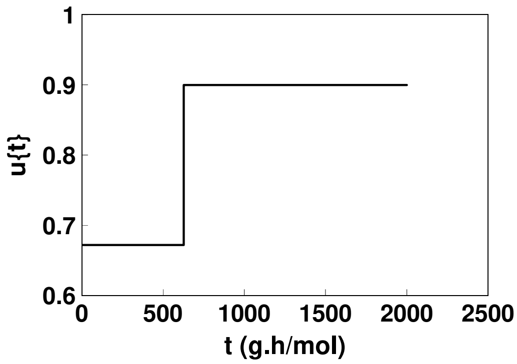

Figure 6. Optimal control for case study V. The associated performance index is $J = 10.0920 \cdot 10^{-3}$.

This problem was solved easily using the ICRS/DS algorithm. As in case study II (which is also highly multimodal), the effect of the parameter k_1 on the SR is important. With a starting profile $\mathbf{u}^0\{t\} = 0.75$ ($J = 6.1509 \cdot 10^{-3}$) , and with $k_1 = 1/3$, the algorithm converged to local optima. However, the SR improved using $k_1 = 1.0$, and with $k_1 = 2.0$ the algorithm converged to the global optimum in all cases. A performance index of $J = 10.0920 \cdot 10^{-3}$, only 0.02 % from the global optimum of Luus and Bojkov (1994), was found in just 5 minutes of CPU time (PC i486/50). The optimal control profile is shown in Figure 6.

7. CONCLUSIONS

The global optimum of difficult multimodal NLPs is obtained easily using the stochastic ICRS algorithm. The method is simple to implement, and the computations are handled easily with low-cost i486 platforms. Regarding dynamic optimization, using the ICRS/DS algorithm, no transformations are required, whereas methods like those based on the maximum principle or those of Cuthrell and Biegler (1989) and Chen and Hwang (1990) require considerable preparation.

Although the five case studies involve few variables and equations, the optimization problems have multiple solutions and discontinuities that are challenging for deterministic algorithms. The stochastic ICRS algorithm appears to efficiently and reliably achieve the global optimum within engineering accuracy in reasonable computation times. For systems involving many more decision variables, the stochastic algorithms are less promising. However, the successes of the ICRS algorithm for the challenging problems reported herein suggest that combinations of stochastic and deterministic methods, with intelligent bounding strategies, are very promising for future development.

Appendix A: Basic CRS algorithm

The basic CRS algorithm is described by Goulcher and Casares (1978) and implemented in the MATLAB program that follows. Note that each time a successful trial has been made, the vector of standard deviations is adjusted according to:

$$\sigma_i = K_1 \Delta x_i \qquad i = 1, ..., n$$

where

$$\Delta x_i = \min\left\{\left|x_i^U - x_i\right|, \left|x_i - x_i^L\right|\right\}$$

and x_i^L and x_i^U are the lower and upper bounds on x_i. Furthermore, after a specified number of failures ($25n$ below), the standard deviations are reduced:

$$(\sigma_i)_{new} = K_2 (\sigma_i)_{old} \qquad i = 1, ..., n$$

The algorithm reports results when

$$\frac{|(x_i)_{new} - (x_i)_{old}|}{x_i^U - x_i^L} \le \epsilon$$

where $\epsilon = 0.0001$ in the MATLAB program.

```
 function [x,funval]=cicrs(x0,lx,ux)
%-- CRS: Controlled Random Search (*basic algorithm*)
%--      x0:  initial point vector
%--   lx,ux:  upper and lower bound vectors for x
  global feasible; global neval;
  nvar=size(x0,2);
%-- Default values for parameters k1, k2 and maxfsd
  k1=1./3; k2=1./2; maxfsd=25.*nvar; error_e=0.0001;
  iter=0; fsd=0; neval=0; x=x0; funval=cfunobj(x0);
  if ~feasible, fprintf('>>> Initial point not feasible'), return, end;
%-- Main loop
 while 1
  iter=iter+1; int_min=min(ux-x,x-lx); sigma=k1.*int_min;
    better=0;
     while ~better
     xnew=x+sigma.*randn(1,nvar);
     if (all(xnew<ux) & all(xnew>lx))
      funval_new=cfunobj(xnew);
       if (funval_new < funval) & (feasible)
        better=1;
       else
        fsd=fsd+1;
         if fsd>=maxfsd
           sigma=sigma.*k2;fsd=0;
          end
        end
     end
  end
     fprintf(' Iter= %5.1f   cFunobj= %12.5f   Neval=%6.1f\n',...
     iter,funval_new,neval);
   if all( abs(xnew-x)/(ux-lx) <= error_e )
     fprintf('*** ICRS has converged ***\n\n')
     x=xnew; funval=funval_new;
     break;
   end
   x=xnew; funval=funval_new; fsd=0;
 end
return

%-- Example of simple objective function with two ineq. constraints
  function [fobj]=cfunobj(x)
   global neval;global factible;
%-- Constraints (declared as if ~expression, return, end )
   feasible=0;
       if ~(1.5+x(1).*x(2)-x(1)-x(2)<=0), return, end
       if ~(-x(1).*x(2)<=10),return, end
   feasible=1;
%-- Objective function
```

```
  fobj= exp(x(1))*(4.*x(1).^2+2.*x(2).^2+4.*x(1).*x(2)+2.*x(2)+1);
  neval=neval+1;
return
```

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